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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Assignee: Johnson Matthey : Filed: 2<sup>nd</sup> December 1999  
Public Limited Company  
Inventors: Martyn Vincent Twigg : Art Unit: 1764  
Application No.: 09/380,864 : Examiner: Jennifer A. Leung

For: EMISSION CONTROL SYSTEM FOR A LEAN-BURN INTERNAL COMBUSTION ENGINE

DECLARATION UNDER 37 CFR 1.132

Assistant Commissioner for Patents  
Washington, D.C. 20231

SIR:

I, Stephen Poulston, being duly sworn, depose and say:

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1. That I presently reside at 4 Hatherley Road, Reading, RG1 5QA, United Kingdom.
2. That I received a Bachelor of Science Honours Degree in Chemistry at The University of Oxford in 1982 and a Ph.D. in Chemistry from Cambridge University.
3. That I have worked for Johnson Matthey plc since 1998 in the field of autocatalysis.
4. That my current position in Johnson Matthey plc is Senior Scientist.
5. That in the course of my research I have found that a 1wt% platinum on alumina catalyst (corresponding to a catalyst loading of approximately 40g Pt/ft<sup>3</sup>) is a more effective lean NOx catalyst than 0.2wt% rhodium on alumina when tested in a synthetic diesel exhaust gas including additional hydrocarbon for two primary reasons. Firstly, the peak NOx conversion is about 35% better. Secondly, the light-off temperature (the temperature at which a catalyst catalyses a reaction with at least 50% efficiency) of the platinum-based catalyst is about 180°C below that of the rhodium-based catalyst.
6. That the conclusions in paragraph 5 above are evidenced by the accompanying graph which shows NO conversion as a function of temperature over a 1wt% platinum on alumina catalyst and a 0.2wt% rhodium on alumina catalyst in a synthetic diesel exhaust gas including additional hydrocarbon having the following composition: 14%O<sub>2</sub>, 3000ppm decane as C1, 750ppm CO, 5%CO<sub>2</sub>, 200ppm NO, 5%H<sub>2</sub>O, N<sub>2</sub> balance. The gas hourly space velocity used was 60,000 litres per hour.
7. That I have read US patent no. 4,071,600 ("the Patent") and see that it shows results for 0.1wt% rhodium on alumina and consider that the Patent teaches that a higher rhodium loading would be desirable but that its use is limited at the date of the Patent by price and availability. Therefore, I would expect from this teaching that 0.2wt% rhodium on alumina

would be more effective than 0.1wt% rhodium on alumina at selectively reducing NO to N<sub>2</sub> by reaction with CO and hydrocarbon.

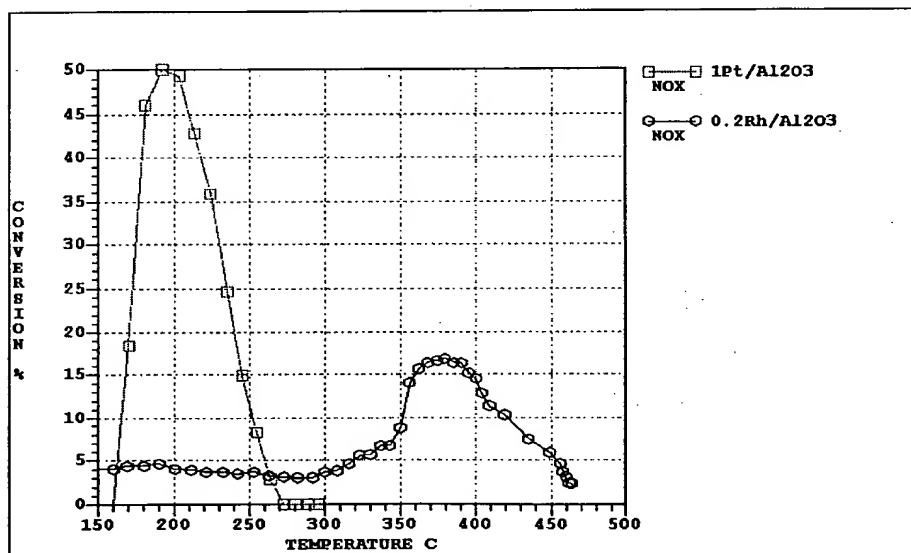
8. That from the results presented in Table 1 in the specification of the above application I would expect the selectivity for the reduction of NO by hydrocarbons and CO over oxidation of the hydrocarbons and CO in oxygen to be improved if the lean NO<sub>x</sub> catalyst consisting of 40g/ft<sup>3</sup> platinum on alumina illustrated in paragraph 5 above was exchanged for a lean NO<sub>x</sub> catalyst consisting of 30g/ft<sup>3</sup> platinum on alumina catalyst.
9. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardise the validity of the above-identified application or any patent issued thereon.

1ST NOVEMBER, 2002

Date

S. Poulton

Stephen Poulston



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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification <sup>6</sup> :<br><b>B01D 53/94</b>   | <b>A1</b>   | (11) International Publication Number: <b>WO 96/39244</b><br>(43) International Publication Date: 12 December 1996 (12.12.96) |
| (21) International Application Number: PCT/GB96/01322<br>(22) International Filing Date: 5 June 1996 (05.06.96)<br>(30) Priority Data:<br>9511412.0                      6 June 1995 (06.06.95)                      GB<br>(71) Applicant (for all designated States except US): JOHNSON<br>MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 78<br>Hatton Garden, London EC1N 8JP (GB).<br>(72) Inventors; and<br>(75) Inventors/Applicants (for US only): FISHER, Janet, Mary<br>[GB/GB]; 14 Tithebam Grove, Calcot, Reading RG31<br>7YX (GB). GRAY, Peter, Geoffrey [AU/GB]; The Linney,<br>Blount's Court Road, Sonning Common, Reading RG4 9RS<br>(GB). RAJARAM, Raj, Rao [MU/GB]; 78 Norfolk Avenue,<br>Slough, Berkshire SL1 3AD (GB). HAMILTON, Hugh,<br>Gavin, Charles [GB/GB]; 12 Rotherfield Way, Caversham,<br>Reading RG4 8PL (GB). ANSELL, Graham, Paul [GB/GB];<br>1 Thornbury Green, Twyford, Berkshire RG10 9RH (GB).<br>(74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Tech-<br>nology Centre, Blount's Court, Sonning Common, Reading<br>RG4 9NH (GB). | (81) Designated States: AU, JP, US, European patent (AT, BE, CH,<br>DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT,<br>SE).<br><br>Published<br>With international search report. |   |
| (54) Title: DIESEL ENGINE EXHAUST GAS PURIFICATION SYSTEM<br><br>(57) Abstract<br><br>The NO <sub>x</sub> emissions from diesel engines may be reduced by incorporating an adsorbent for unburnt fuel in the exhaust, together with a lean NO <sub>x</sub> catalyst. The adsorbent adsorbs unburnt fuel during cooler parts of the engine operating cycle, and releases it during hotter parts of the cycle, so that it is effective to reduce NO <sub>x</sub> .   |   |   |

**Diesel engine exhaust gas purification system.**

The present invention concerns improvements in emission control, more especially, it concerns improvements in the control of regulated emissions from diesel engines.

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Light duty diesels, for example those of up to about 2.5 litre capacity used in private cars and light vans, show much better fuel economy and hydrocarbon emissions than gasoline engines and are increasing in number. Emissions from diesel engines are now being regulated by legislation, and whilst hydrocarbon emissions do not present a problem in meeting emission limits, NO<sub>x</sub> is problematical. Since the exhaust gases from lean-burn engines such as diesels are high in oxygen content

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throughout the cycle of operation, it is more difficult to reduce NO<sub>x</sub> to N<sub>2</sub>. A contribution to this problem is the low exhaust gas temperature in comparison to gasoline-fuelled engines, which can also vary quite dramatically according to operating conditions. Thus, for a state of the art diesel exhaust catalyst system, 50% of hydrocarbons are oxidised at a temperature in the range 190 to 250°C, and this inclines to 100% at higher temperatures. The conversion of NO<sub>x</sub>, however, shows very different characteristics, with a marked peak, creating a "window" of conversion at the 30 to 60% level, at a range of temperatures depending upon the catalyst system and engine system. This is illustrated in accompanying Figure 1. As mentioned, the exhaust gas temperature will vary over a test cycle, so that the catalyst is seldom at a suitable temperature for optimum conversion. Over a test cycle therefore, the cumulative conversion efficiency for diesel NO<sub>x</sub> may only be about 10%. In fact, as the catalyst temperature drops below the peak conversion temperature for NO<sub>x</sub>, the temperature is also below "light off" for HC conversion. Accordingly, most of the unburnt hydrocarbons go out the tail pipe unreacted, along with unconverted NO<sub>x</sub>. It is to be noted that the exhaust temperature with heavy duty diesels is much higher and therefore these do not face quite the same problems. Nonetheless, the present invention offers improvements in emission control particularly during start-up of heavy duty diesel engines, and offers the potential to control emissions to meet expected future regulations.

It is an aim of the present invention to provide a diesel engine system capable of a substantial reduction in emissions of NO<sub>x</sub>, especially but not exclusively from light duty diesel engines.

Herein, diesel engines are those fuelled by fuel oil of the type often known as "gas-oil". The invention may also be applied to diesel compression ignition engines fuelled by other fuels including oxygenated fuels.

5 We would mention GB Patent 1407772 (Nissan), which concerns an internal combustion engine fitted with a three-way catalyst, and teaches a complicated system which includes supplying additional fuel into the exhaust upstream of the catalyst, in order to assist in the reduction of NO<sub>x</sub> to N<sub>2</sub>. The skilled person considers that the teaching of this patent is only relevant to gasoline-fuelled engines. There is no  
10 suggestion that unburnt fuel may be collected from the exhaust gas instead of the supply of additional fuel upstream of the catalyst.

WO 94/22564 (Engelhard) describes a catalyst composition for treating diesel engine exhausts, comprising a ceria component and a catalytically active amount  
15 of a zeolite. The purpose of this catalyst composition is stated to be the oxidation of volatile fractions, and the catalyst is operated under oxidising conditions, and is completely unconcerned with levels of NO<sub>x</sub>.

The present invention provides a diesel engine system which exhibits  
20 a higher exhaust gas temperature and a lower exhaust gas temperature, said lower temperature being insufficient for significant catalytic conversion of NO<sub>x</sub> to N<sub>2</sub>, and a lean NO<sub>x</sub> catalyst system comprising lean NO<sub>x</sub> catalyst and an adsorbent for unburnt fuel, arranged and constructed so that during the lower exhaust gas temperature parts of the engine operating cycle, the adsorbent adsorbs unburnt fuel, and during the higher

exhaust gas temperature parts of the operating cycle, the adsorbent releases unburnt fuel, which combined with unburnt fuel in the exhaust gas, is effective to increase the conversion of NOx.

5                   The invention further provides a method of increasing the conversion of NOx in a diesel engine fitted with a catalyst system, which catalyst system comprises a lean NOx catalyst and an adsorbent for unburnt fuel, comprising permitting said adsorbent to adsorb unburnt fuel from the exhaust gases, during parts of the engine operating cycle in which the exhaust gases are cooler and permitting said adsorbent to  
10                   desorb unburnt fuel during parts of the operating cycle in which the exhaust gases are hotter, whereby the conversion of NOx is increased in aggregate over a total operating cycle.

                  It is recognised that the use of adsorbent has been recommended for  
15                   gasoline engines. However, the emission characteristics of gasoline engines are very different from those of diesel engines. In particular, unburnt fuel is particularly a problem during cold starts of gasoline engines, that is before the catalyst lights off. Unburnt fuel emissions from the first few minutes of operation may dominate the aggregate emissions over a test cycle. Accordingly, for gasoline engines, an adsorbent  
20                   acts to adsorb unburnt fuel during cold start, and releases it once the catalyst has reached light-off, for oxidation. After light-off there is no actual need for the adsorbent, especially as the gasoline engine and catalyst system does not cycle significantly through cooler parts of the operating cycle during operation. Since diesel engines do not have any great difficulty meeting the regulated emission levels for

unburnt fuel, there is no reason to use an adsorbent to reduce hydrocarbon levels in exhaust gases. In the present invention, the adsorbent is used to accumulate hydrocarbon in order to reduce NOx emissions during parts of the operating cycle, and we believe this to be a wholly novel concept. The characteristic cycling of exhaust gas temperature in diesel engines during FTP or ECE tests is important to the operation of the present invention. If the exhaust gas was at "steady state" the adsorbent would eventually saturate and there would not be an overall improvement in NOx conversion. The cycling permits the adsorbent to adsorb unburnt fuel during the cool part of the cycle when there would be little catalytic conversion of NOx and to desorb unburnt fuel during the hotter part of the cycle (simultaneously regenerating the adsorbent), in order to convert NOx when the catalyst is at a higher temperature.

It will be readily understood by the skilled man that "hotter" and "cooler" or equivalent terminology used herein is with reference to the average exhaust gas temperature, and that there are clear cycles from lower temperatures to higher temperatures during emission tests. These cycles are shown in accompanying Figure 2. Desirably, the adsorbed fuel is desorbed during maximum conversion of NOx to N<sub>2</sub>, which is, for most state-of-the-art Pt-containing lean-NOx catalysts, at catalyst temperatures of from 190 to 250°C.

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The adsorbent may be any adsorbent capable of reversibly adsorbing the particular fuel or unburnt by-products under operating conditions, and may conveniently be a zeolite. There are a variety of zeolites which are capable of performing this duty, including non-metallised zeolite such as ZSM-5, ion-exchanged



or metal impregnated ZSM-5, and zeolite in which the silica to alumina ratio is very high, such as silicalite. Metallised or non-metallised zeolite, *eg* mordenite, Y and  $\beta$  zeolite may be used. It may be desirable to incorporate a metal, especially cobalt, platinum or one of the other platinum group metals, or a rare earth, in the adsorbent, and in some cases, this may improve cleaning of the adsorbent surface during regeneration. The particle size and pore size may be adjusted or chosen in order to improve trapping and release characteristics for the hydrocarbon molecules. Combinations of zeolites may also be beneficial.

The catalyst chosen may be one of the class generally known as diesel catalysts, or lean NO<sub>x</sub> catalysts, and may be, for example, a Pt on an alumina, alumina-zirconia, zirconia, sulphated zirconia, silica-alumina, silica, titania, silica-titania or tin oxide-alumina support system. The Pt may be combined with another catalytic or promoting metal, *eg* Pt-Co, Pt-Ru, Pt-Ir, Pt-Rh or Pt-Pd, on any of the above supports or on a zeolite, *eg* ZSM-5. Other lean NO<sub>x</sub> catalysts such as Cu on ZSM-5 may be used, and the exact nature is not believed to be critical to the operation of the present invention.

The catalyst is preferably carried on a catalyst support substrate, *eg* a metal or, preferably, a ceramic monolith of the honeycomb flow-through type, and may be on a separate monolith from the adsorbent. It may be desirable, however, that both catalyst and adsorbent are deposited on the same monolith. Suitably, for example, a standard cordierite monolith is washcoated with a slurry of high surface area alumina, then is dried and fired. The coated monolith may then be impregnated with

catalytically active components, *eg* a solution of one or more platinum group metal salts or compounds, and dried and fired. An outermost layer of adsorbent may be applied by washcoating with a slurry of the adsorbent together with a supplemental adherence modifier such as a colloidal silica material, *eg* that known as "Ludox". The adsorbent may, for example, form 67% by weight, on a dry basis, of the slurry, and the silica material forms 33% by weight, on a dry basis. It may be necessary to apply each washcoat several times, in order to obtain the optimum loading for the particular system. Alternatively, similar coating and impregnation may be used to apply the adsorbent to the washcoated monolith, then a further washcoat of alumina before the catalyst is applied as the outermost layer. If desired, the adsorbent and catalyst may be applied in a single, mixed layer. The skilled man may adapt the invention as described herein without departing from the inventive scope.

The nature of the present invention will be better appreciated with reference to the accompanying drawings, in which

Figure 1 is an illustration of HC and NO conversion over a catalyst plotted against gas temperature.

Figure 2 illustrates the gas temperature at the inlet to a catalyst in a diesel Volkswagen Golf on the FTP test cycle, and

Figures 3 to 6 are traces of NO<sub>x</sub> conversion in a simulated engine operation.

Referring to Figure 1, it can be seen that NO conversion reaches a sharp peak at about 200°C. Over much of the temperature range, NO conversion was below 10%. At peak NO conversion, the conversion of HC is less than maximal.

5                   Considering the FTP plot (Figure 2) it can be seen that much of the time, the gas temperature at the inlet to the monolith is between 150 and 200°C, during which there is very low conversion of NO and HC.

10                   Figure 3 represents the results from testing a model diesel exhaust gas (400ppm NO<sub>x</sub>, 800ppm C<sub>3</sub>H<sub>6</sub>, 12% O<sub>2</sub> balance N<sub>2</sub>) in a transient test rig which modelled exhaust gas temperatures according to a cycle typical of the middle section ("cold stabilised") of a FTP test cycle. The exhaust gas was fed to a catalyst system according to the invention, composed of a commercial diesel catalyst (1 part by weight) admixed with zeolite ZSM-5 (1 part by weight). A peak NO<sub>x</sub> conversion of about 60%  
15                   was observed, compared to a peak of about 30% for a control experiment using the same catalyst, without zeolite. In addition, it is believed that the width of the NO<sub>x</sub> conversion trace is increased.

20                   Figure 3 shows a dip between two peaks. This is believed to be caused by the catalyst heating up to a temperature above the peak NO<sub>x</sub> conversion temperature.

Further tests have been carried out to compare the performance of 0.3g of 1wt% platinum on alumina powder which is blended with a further amount of

alumina (0.3g), with the same platinum on alumina powder blended with 0.3g of ZSM-5 adsorbent. A modified FTP test for diesel engines, representing the middle section of the test, during which the exhaust gas temperature cycles between about 170°C and 240°C, was performed. and the results are shown in Figure 4. The lower set of traces show NOx conversion for the catalyst and ZSM-5 blend, and a standard calculation carried out by computer shows an average NOx conversion of 33.4%. The upper set of traces, for the catalyst and alumina powder, shows an average NOx conversion of 21.0 %. In both sets of traces, the broken line represents temperature.

The test gas used in these tests, and in the following tests, was a model diesel exhaust consisting of 400ppm propane, 200ppm NOx (NO), 4.5% CO<sub>2</sub>, 200ppm CO, 20ppm SO<sub>2</sub>, 5% water vapour, 12.5% O<sub>2</sub> and the balance being N<sub>2</sub>.

Additionally, the same test was carried out using a catalyst system more representative of a commercial system, that is a standard cordierite catalyst carrier, in the form of a monolith of 1 inch diameter and 1.5 inch length (25.4mm diameter, 38.1mm length), having 400 cells per square inch (400 cells/645.16mm<sup>2</sup> or 0.62 cells/mm<sup>2</sup>). The monolith carried 3g per cubic inch (3g/16.39cm<sup>3</sup> or 0.18g/cm<sup>3</sup>) of washcoat, which was either alumina or a 50/50 mixture of alumina and ZSM-5. The washcoated monolith carried platinum in an amount of 70g/cubic foot of catalyst volume (70g/28.32 litres or 2.5g/litre). The average NOx conversion for the present invention, catalyst and adsorbent, was 29.4% (lower traces), whereas the average NOx conversion for the standard catalyst system was 16.4% (upper traces), and the results are shown in Figure 5. In both sets of traces, the broken line represents temperature.

For both of the above tests, the average NO<sub>x</sub> conversion is much improved by the incorporation of an adsorbent.

5       The identical monoliths and powders used in the last-mentioned tests, were used for tests measuring NO<sub>x</sub> conversion, when the model exhaust gas was heated at a linear heating rate of 50°C/minute. The results are shown in Figure 6, the upper set of traces being for the monoliths, and the lower set of traces being for the powders. In both sets of traces, the continuous line represents conversion by the catalyst and adsorbent, whereas the broken line represents conversion by the catalyst and alumina.

10       In both cases, there is a very substantial improvement in peak NO<sub>x</sub> conversion and in aggregate NO<sub>x</sub> conversion, as shown by the areas under the curves, for the catalyst systems used in the present invention.

15       In all cases, NO<sub>x</sub> conversion was measured using a chemiluminescent analyser.

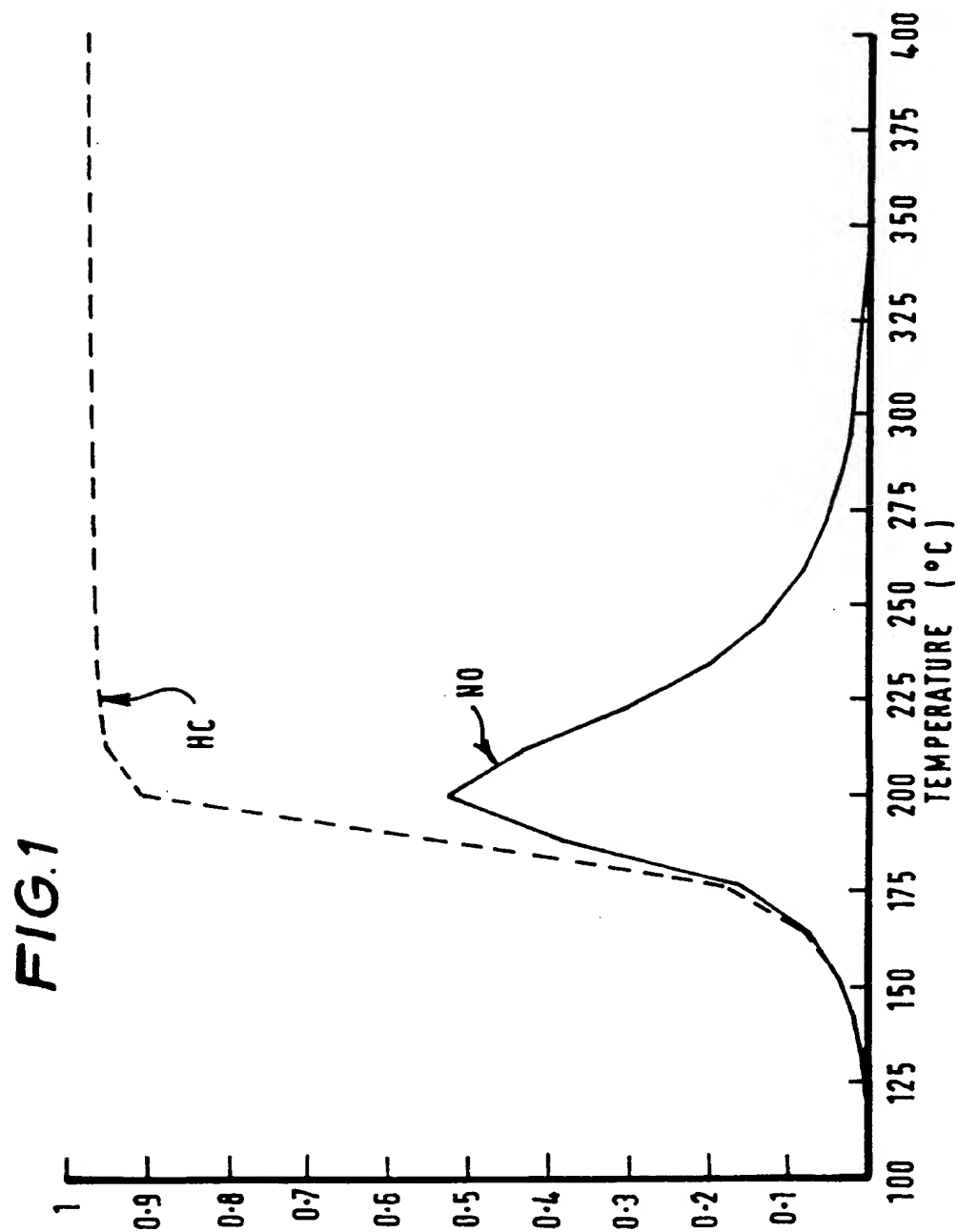
**CLAIMS**

1. A diesel engine system which exhibits variation between a higher exhaust gas temperature and a lower exhaust gas temperature, said lower temperature being insufficient for significant catalytic conversion of NO<sub>x</sub> to N<sub>2</sub> and a lean NO<sub>x</sub> catalyst system comprising a lean NO<sub>x</sub> catalyst and an adsorbent for unburnt fuel, arranged and constructed so that during the lower exhaust gas temperature parts of the engine operating cycle, the adsorbent adsorbs unburnt fuel, and during the higher exhaust gas temperature parts of the operating cycle, the adsorbent releases unburnt fuel, which combined with unburnt fuel in the exhaust gas, is effective to increase the conversion of NO<sub>x</sub>.
2. A system according to claim 1, wherein the adsorbent is a metallised or non-metallised zeolite.
3. A system according to claim 1 or 2, wherein the catalyst is a platinum-based catalyst on an oxide or zeolite support.
4. A system according to any one of claims 1 to 3, wherein the diesel engine is a light duty diesel.
5. A system according to any one of the preceding claims, wherein the adsorbent is effective to desorb unburnt fuel in the temperature range 190 to 250°C.

6. A method of increasing the conversion of NO<sub>x</sub> in a diesel engine fitted with a catalyst system which catalyst system comprises a lean NO<sub>x</sub> catalyst and an adsorbent for unburnt fuel, comprising permitting said adsorbent to adsorb unburnt fuel from the exhaust gases during parts of the engine operating cycle in which the exhaust gases are cooler and permitting said adsorbent to desorb unburnt fuel during parts of the operating cycle in which the exhaust gases are hotter, whereby the conversion of NO<sub>x</sub> is increased in aggregate over a total operating cycle.

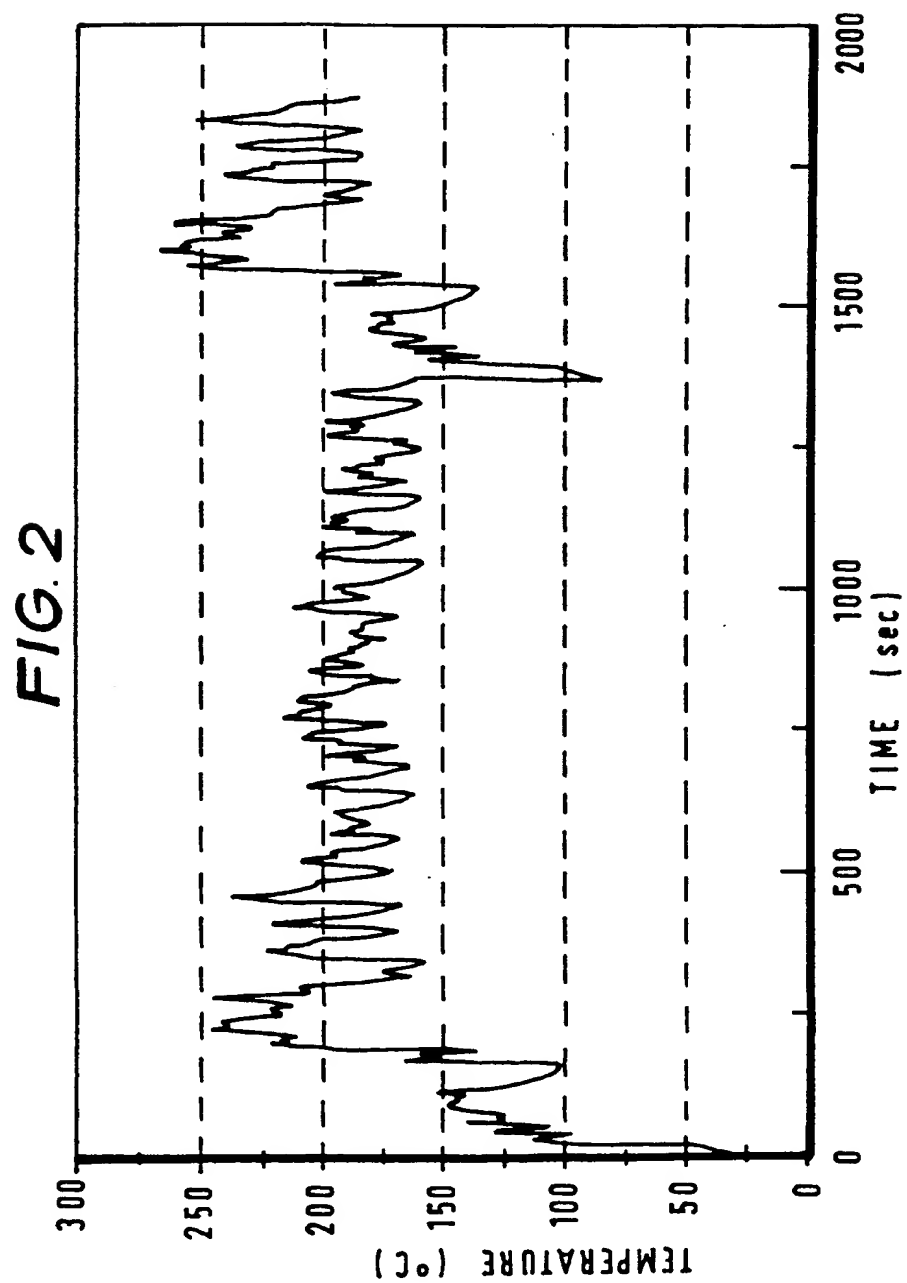
7. A method according to claim 6, wherein the adsorbent is effective to desorb unburnt fuel in the temperature range from 190 to 250°C.

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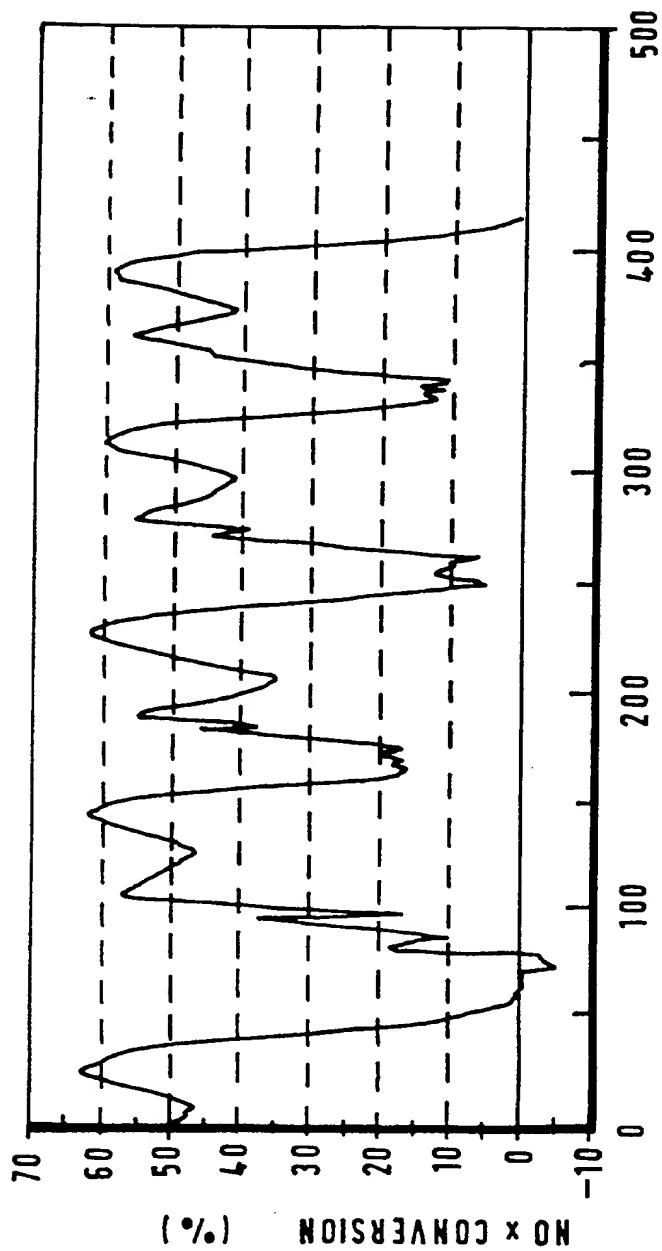
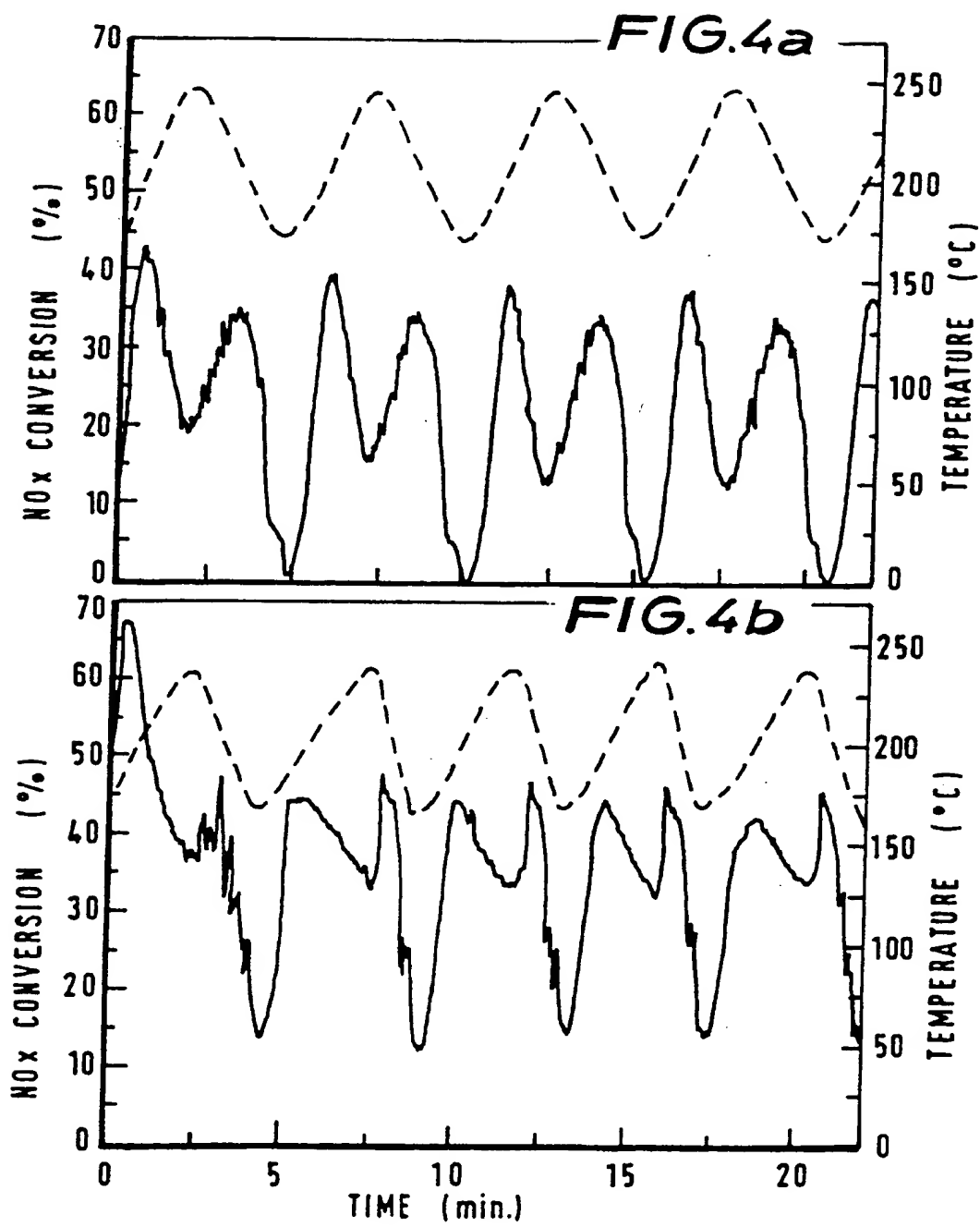
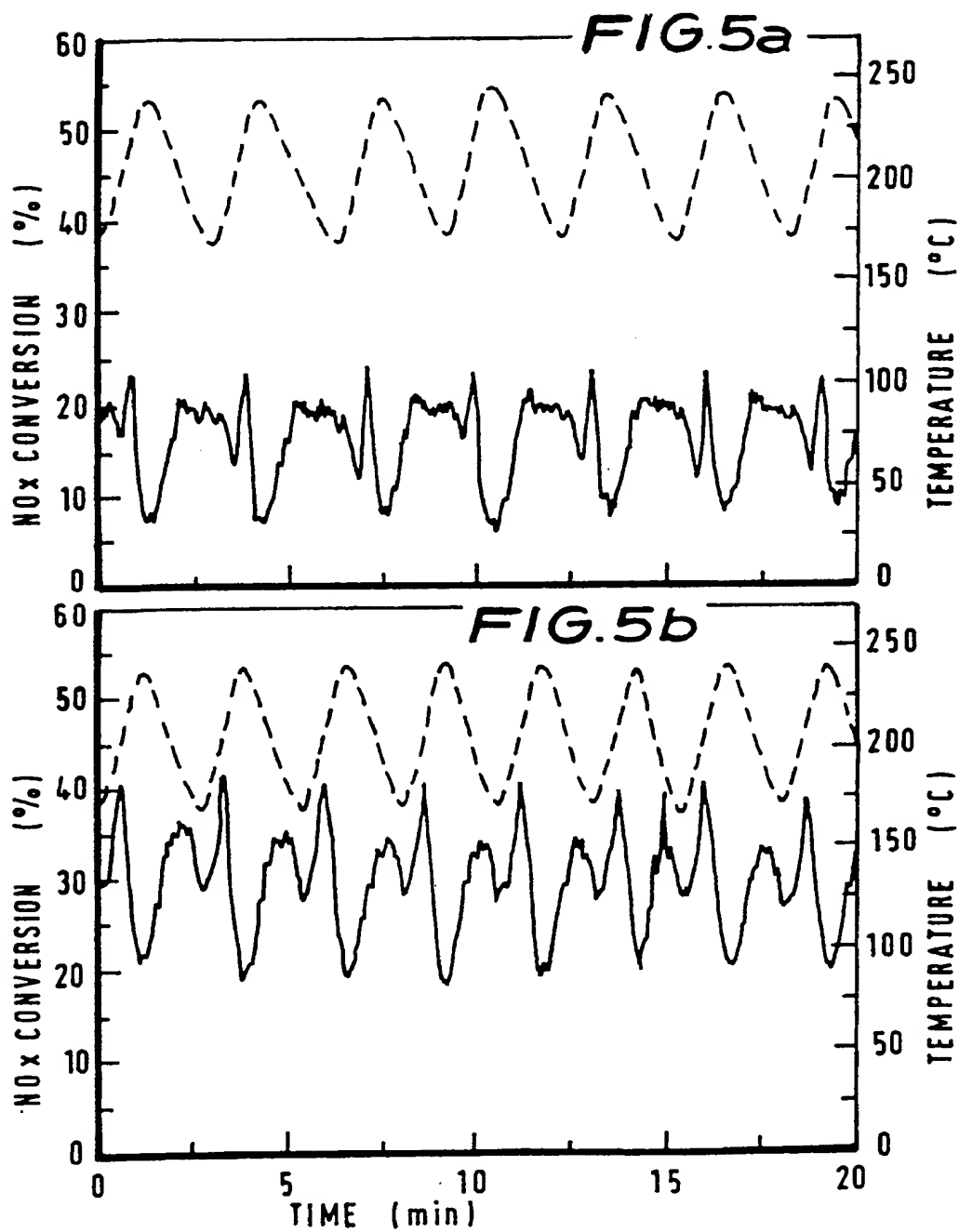


FIG.3

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